

REPROCESSING OF USED TIRES INTO ACTIVATED CARBON AND OTHER PRODUCTS

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ABSTRACT

The disposal of used tires generated each year in the U.S. by landfill is increasingly becoming an unacceptable solution. A better solution from an environmental and economic standpoint is to thermally reprocess the tires into valuable products such as activated carbon, other solid carbon forms (carbon black, graphite, and carbon fibers), and liquid fuels. In this study, a high surface area activated carbon ($> 800 \text{ m}^2/\text{g}$ solid product) was produced in relatively high yields from pyrolysis of tires up to 900°C , followed by activation in CO_2 at the same temperature. The surface area of this carbon is comparable with that of commercial activated carbon. The efficiency of the activation process (gain in specific surface area/loss in mass) was greatest when the pyrolysis was done on unground pieces of tire. This approach was found to give the best results for the preparation of activated carbon from used tires, with a total surface area production as high as $138 \text{ m}^2/(\text{g}$ original tire). Oxygen pretreatment of tires appears to increase both the yield and surface area of carbon produced from this system. High pressure treatment of tires at low temperatures ($< 400^\circ\text{C}$) is an alternative approach if recovery of carbon black or fuel oils is the primary objective.

INTRODUCTION

The disposal of 280 million tires generated each year in the U.S. by landfill is increasingly becoming an unacceptable solution [1]. The tires take up large amounts of valuable landfill space and also represent a fire hazard. Recently, a large mountain of tires caught on fire in Canada with widespread environmental consequences due to the oils and gases generated from the decomposing tires. A better solution from an environmental and economic standpoint is to thermally reprocess the tires into valuable products [2]. The largest scale efforts employ tires either as a fuel [3] or as a filler for asphalt [4]. These two technologies consume about 5-6 million tires annually. However, tire burning has had repeated problems with feeding the tires and slagging, while the rubber asphalt costs 40% more than conventional material. An alternative is to reprocess the used tires into activated carbon and other solid carbon forms (carbon black, graphite, and carbon fibers), and liquid fuels. The key to producing such a product is controlling the chemistry of low temperature carbonization, which is the subject of this paper.

Pyrolysis has been widely used for converting solid fossil fuels, e.g. coal, into liquid and gaseous hydrocarbons, a process which results in a solid char residue. Coal pyrolysis has been extensively studied [5-7]. Used automotive tires contain polymeric aromatic structures which are similar to those of coal in some respects. Therefore, pyrolysis of waste tires to produce valuable products is currently receiving some attention. However, investigations of tire pyrolysis are rarely reported in the open literature.

The most commonly used vulcanized tire rubber is a styrene-butadiene-copolymer (SBR) containing about 25 wt.% styrene [8]. A typical composition for tire rubber is shown in Table 1. Also, a comparison of the structure and composition of tire rubber with that of a bituminous coal is shown

in Fig. 1. In most cases, tire pyrolysis studies were performed under inert conditions [8,9,10]. However, pyrolysis may be carried out in mildly oxidizing atmospheres, such as steam and carbon dioxide, to improve the quality of pyrolytic products [11,12,13].

Tire pyrolysis experiments have been conducted in the 500-900 C° range [8,9,11]. Similar to coal pyrolysis, the principal products from tire pyrolysis are gases, liquid oils and solid carbon residues. The following yields (as-received basis) of tire pyrolysis are typical: 33-38 wt.% char, 38-55 wt.% oil, and 10-30 wt.% gas. The product yields are affected by the pyrolysis conditions, such as pyrolysis temperature and heating rate. The literature work on the analysis of products from tire pyrolysis is summarized as follows:

Gas Analysis - Gases produced from tire pyrolysis are mainly hydrogen, carbon dioxide, carbon monoxide, methane, ethane and butadiene, with lower concentrations of propane, propene, butane and other hydrocarbon gases [8]. The temperature for the maximum evolution rate of each gas shifts to higher temperature levels as heating rate is increased. There was an increase in the total gas emission with heating rate and a corresponding decrease in oil yield [8]. Pyrolysis carried out in the presence of water increases the production of hydrogen and carbon monoxide [11]. This is thought to result from the occurrence of carbon gasification by steam, i.e., $C + H_2O \rightarrow CO + H_2$.

Oil Analysis - The yield of oil from tire pyrolysis is high (~50 wt % of initial tire rubber), reflecting the potential of tire rubber as a substitute for fossil fuel and chemical feedstocks. The oils have high aromaticity, low sulfur content, and are considered relatively good fuels [13]. The molecular weight range of the oils was up to 1600 with an average molecular weight in the 300-400 range [8]. The average molecular weight increases with increasing pyrolysis temperature and with decreasing heating rate. Infrared analysis of the oils indicated the presence of alkanes, alkenes, ketones or aldehydes, aromatic, polyaromatic and substituted aromatic groups [8]. An increase in pyrolysis temperature produced a decrease in the aliphatic fraction and an increase in the aromatic fraction [8]. Aliphatic hydrocarbons and alkylbenzenes are the major components of the oil if the pyrolysis is performed in the presence of water [11], and the average molecular weight of the aliphatic hydrocarbons was 164 and that of alkylbenzenes was 180. These average molecular weights are lower than the values for the oils from tire pyrolysis under an inert environment. This may indicate that the cracking of oil molecules during pyrolysis is promoted by the introduction of water.

The oil product from tire pyrolysis is a potential source of energy and chemicals. The oils may be used directly as fuel or added to petroleum refinery feedstocks [8]. The composition of the gasoline boiling fraction was reported to be comparable to that of petroleum gasoline [13]. The derived oils may also be an important source of refined chemicals, because it has been reported that they contain high concentrations of valuable chemical feedstocks, such as benzene, toluene and xylene [8].

Carbon Residue Analysis - The carbon residue would become a marketable product if its properties are similar to those of manufactured carbons. The simultaneous production of valuable solid products and gaseous and/or liquid fuels from what is currently a waste material would make tire pyrolysis economical if a large supply is readily available. This situation exists in many regions of the U.S.

Tire pyrolysis performed in an inert environment can produce 33-38 wt. % of carbon residue, as mentioned previously. It has been reported that the char yield increases with decreasing pyrolysis temperature and decreasing heating rate [8]. The surface area of the tire char also depends on pyrolysis temperature and heating rate. Williams et al. [8] reported that the surface area of the tire chars increases with both pyrolysis temperature and heating rate. However, Petrich [9] claims that chars prepared at too low of a temperature retain a large fraction of volatile material, resulting in lower surface areas, and those prepared at too high of a temperature tend to sinter and lose surface area. The surface area of a tire char produced by pyrolysis in an inert gas usually ranges from 30 to 90 m²/g [8,9,11].

Basically, there are two uses of tire chars: as a reinforcing filler and an adsorbent. Usually commercial carbon black is used for filling polymers and vulcanizates. Use of the tire char as an end product for the tire and printing ink industries has been reported to be unsatisfactory [8,9]. This is due to the high ash content of the tire char. Chars from tire pyrolysis contain as much as 15 wt. % of ash, with the majority of this ash being zinc oxide [9]. A means of removing the ash from tire char is an important issue in the process of producing useful carbon black from waste tires.

Carbon as an adsorbent is usually evaluated by its surface area. Measurement of surface area can be obtained by a gas adsorption method, for example nitrogen BET. Tire chars which had not been activated served well in removing mercury compounds from aqueous solution [13]. As mentioned above, the surface area of tire char is in the range of 30-90 m²/g, which is comparable with those of carbon blacks used in rubber products [8]. However, these values are too low for use of the char as activated carbon since commercial activated carbons have surface areas of around 1000 m²/g [8,9,11]. Therefore, an activation process is required to produce activated carbon from tire char. Carbons can be activated by mild oxidation with steam or carbon dioxide at high temperatures to develop internal surface area. The slow gasification kinetics of carbons in steam or carbon dioxide allows gas molecules diffusing into the carbon micropores to create or enlarge micropores. The activation process usually follows hydrocarbon pyrolysis performed in an inert environment, but it is possible to accomplish pyrolysis and activation in one stage by pyrolyzing under mildly oxidizing conditions [11].

Torikai et al. [10] pyrolyzed tires at 550°C for 30 minutes and activated the granulated char with CO₂ at 900°C. They found linear relationships between activation time and burn-off, burn-off and surface area, and burn-off and Methylene Blue value (an adsorption test). This activated carbon had a surface area up to 400 m²/g.

Ogasawara et al. [11] carried out the pyrolysis and activation of tires in one stage. In their study, water was continuously introduced to the sample with helium. The carbon residue from 1 hour steam activation at 900°C had a surface area of 1260 m²/g, while pyrolysis in helium gave a char with a surface area of 87 m²/g. The carbon residue produced from this "wet method" is as good as the commercial activated carbon in terms of surface area, but the carbon yield was only 9 wt. % of the starting tire.

In studies on coal liquefaction and pyrolysis [14,15], it has been found that oxygen functional groups, such as carboxyl and hydroxyl appear to play a major role in promoting the crosslinking reactions between molecules in coal. These crosslinking reactions are usually encountered at low temperatures (< 200°C) prior to the occurrence of bond cleavage in liquefaction or pyrolysis. A lot of effort has been devoted to the reduction of oxygen functions of coal in order to increase the liquid yield for coal liquefaction. Conversely, an increase of the oxygen functional group content would be expected to result in an increased char yield from pyrolysis of coal.

In the study of tire pyrolysis, some workers [10,11] have already produced high surface activated carbons from tire chars. However, the product yields of their systems were very low, and this is a serious drawback from economic point of view. Therefore, a method to increase the char yield from tire pyrolysis is one of the most important issues in making activated carbon from waste tires. Since the chemical structures in the tire rubber are similar to structures found in the coal, an increase of the oxygen functional group content in tires would be expected to promote the crosslinking reactions between tire molecules, and thus enhance the char yield in pyrolysis. In this study, oxygen pretreatment of tires was carried out prior to pyrolysis, and the results were compared to those without oxygen pretreatment.

High pressure treatment of coal under wet (steam) conditions, has been reported to allow the breaking of hydrogen bonds, loosening of the coal matrix and stabilization of some of the reactive components of the coal [16]. The extraction of oils from tires by supercritical or subcritical water was

studied by Funazukuri et al. [12]. Under the current study, a limited number of runs was done on low temperature, high pressure treatment of tires under wet or dry conditions to study the "self-liquefaction" of tires to recover the carbon black and provide liquid fuels simultaneously.

EXPERIMENTAL

There were two tire samples used in this investigation: granulated and non-granulated. The granulated sample was prepared by crushing and grinding a large piece of frozen tire under cryogenic conditions. The particle size of the sample was -50 mesh. The non-granulated sample was prepared by cutting the tire rubber into a fixed size of 170 ± 5 mg, unless otherwise specified.

Most of the tire pyrolyses were carried out in a TG-FTIR system under an inert (helium) or a mildly oxidizing (carbon dioxide) environment [17]. Tire char produced from a fixed-bed reactor under an inert environment was prepared to compare with that produced from the TG-FTIR system. Flash pyrolysis of tire was also performed in a wire-grid reactor with direct electrical resistance heating in helium. The heating rate was as high as $20,000^{\circ}\text{C}/\text{min}$.

Various treatments of the tires were investigated in order to improve the quality of products. The granulated sample was used for these treatments. The tire treatment procedures are briefly described as follows: 1) Oxygen pretreatment: Sample was kept in the air at 140°C for 15 days; 2) Wet high pressure treatment: Sample was treated with water in an autoclave at 4000 psig and 400°C for 30 min.; 3) Dry high pressure treatment: Sample was enclosed in a 3500 psig helium filled autoclave at 400°C for 30 min.

The gases evolved during pyrolysis can be quantitatively measured in the TG-FTIR system [17]. The liquid oil product was analyzed as KBr pellets in a Nicolet FT-IR. For quantitative analysis of the oil FT-IR spectra, a curve analysis program is employed to synthesize the IR spectra [18-21]. The quantitative data derived from the spectral synthesis gives a good quantitative determination for aliphatic, aromatic, ether, carboxyl and hydroxyl functional groups and a qualitative determination of alkanes and alkenes [18-21].

The solid residues produced under various pretreatment and pyrolysis conditions were subject to surface area measurements. The measurements were carried out using a dynamic, continuous method. A commercial instrument (Quantasorb, Quantachrome Corp.) was used to determine N_2 BET surface areas. Prior to surface area analysis, all samples were outgassed in a flow of nitrogen at 300°C for 1 hour. The N_2 surface area was determined at 77 K.

A scanning electron micrograph (SEM) with an x-ray analysis instrument was used in this study to investigate the surface structure and sulfur content of different samples.

Tire chars produced from pyrolysis were activated in a flow of CO_2/He mixture at 900°C . The CO_2 partial pressure during activation was fixed at 0.08 atmosphere, unless otherwise specified. The activated chars with various burn-offs were prepared and subject to surface area analysis.

RESULTS AND DISCUSSION

1. Tire Sample Analysis

The results of proximate and ultimate analyses of the granulated tire are shown in Table 2. Since the ash content shown in Table 2 is higher than for the unground sample and those reported in the literature [8,11], it was concluded that the granulated tire sample was accidentally contaminated in the grinding and/or sieving process. By SEM/x-ray analysis, the contamination was found to be mainly iron. The non-granulated tire sample, which was not contaminated, has an ash content around 2.9 wt.%. This

is similar to what has been reported previously for tires [8,11]. The ash free composition of the non-granulated tire sample is the same as that of granulated sample shown in Table 2. The samples were supplied by Prof. Mark Petrich of Northwestern University from a batch of shredded (used) truck tires.

2. Product Composition from Tire Pyrolysis

Gas Products - The typical product evolution data during granulated tire pyrolysis, starting from room temperature with a heating rate of 30°C/min up to 900°C, are shown in Fig. 2. The principal gases evolved are H₂O, CH₄, CO₂, CO, SO₂, C₂H₄, and NH₃. The total yield of gases and tars increases with temperature up to 650°C, after which there is no significant change in product yield. Tar is the major product of tire pyrolysis. It evolves mainly between 350 and 500°C.

The product evolution during the pyrolysis of the oxygen treated sample is shown in Fig. 3. It is of interest to notice, by comparison of Fig. 3 with Fig. 2, that the gas yields during pyrolysis were significantly increased by oxygen pretreatment, whereas the tar yields were reduced. The comparison of the product yields of these two samples is shown in Table 2. There was no surprise to see the enhanced evolution of H₂O, CO, CO₂ and SO₂ due to oxygen pretreatment, since oxygen would react with the components in the tire, and result in the increase of oxygen containing products from pyrolysis. However, the interpretation of the observations of the increased evolution of CH₄ and C₂H₂ and the reduced production of tars resulting from oxygen pretreatment is not as straightforward. It has been reported that oxygen plays a major role in crosslinking and cleavage of the network structure of coals [14,15]. Our results obviously revealed that oxygen pretreatment promoted the cleavage reactions for producing small molecules, such as CH₄ and C₂H₂, and the crosslinking between macromolecules in tires to reduce tar evolution, with a corresponding increased char yield (see below). This is a very beneficial result for tire carbonization process, since the char yield is significantly raised (see Table 3) due to the crosslinking between macromolecules, whereas the production of gaseous fuels, CH₄ and C₂H₂, is also promoted.

Liquid Products - The condensable liquid products (tars) are the major products of tire pyrolysis. The compounds found in tire pyrolysis oils have been identified as largely consisting of benzene, toluene, xylene, styrene, indane, indene, naphthalene, methyl naphthalenes, biphenyl, fluorene, pyrene, anthracene, phenanthrene and various other 3, 4, 5 and 6 ring polyaromatic hydrocarbons and aliphatic compounds, including alkanes and alkenes [8]. Since the compounds in the oil are too numerous and diverse to recognize quantitatively, functional group compositional analysis was used to more clearly reveal the properties of the oil. The FT-IR absorbance spectrum of the tire oil is shown in Fig. 4. As shown in Fig. 4, the aliphatic C-H stretching vibrations at 2930 and 2850 cm⁻¹ and C-H deformation vibrations at 1350-1470 cm⁻¹ indicate the presence of alkanes. The C-H stretching at 3000-3100 cm⁻¹, 1600 and 1500 cm⁻¹ carbon-carbon stretching vibrations, C-H in-plane bending in the 1000-1100 cm⁻¹ region, and 700-900 cm⁻¹ (C-H out of plane bending) peaks indicate the presence of aromatic compounds. The C=O stretching vibrations at 1700 cm⁻¹ indicate the presence of ketones or aldehydes. The 1630 and 990 cm⁻¹ absorbance peaks are indicative of alkenes. The O-H stretching vibrations between 3200 and 3600 cm⁻¹ indicate the presence of hydrogen-bonded alcohols or phenols. The C-O stretching in the 1060-1300 cm⁻¹ range indicates the presence of alcohols, ethers, and carboxylic acids. The quantitative functional group analysis of the oil based upon the absorbance spectra in Fig. 4 is summarized in Table 4. It is indicated in Table 4 that the oils formed are mostly aliphatic.

Solid Products - The solid residue yield varied with pyrolysis conditions. The product yields of tire pyrolysis in helium under different pyrolysis conditions are shown in Table 5. These results show that the char yield increases with decreasing pyrolysis temperature. This is consistent with the results of other workers [8,11,12]. Table 5 also shows an increasing char yield with increasing heating rate, and this trend is opposite to that reported by Williams et al. [8]. This disagreement is probably due to the absence of a holding period at the final pyrolysis temperature in our study, whereas there was at least two hours of holding time at final temperature in the work of Williams et al. [8].

Tire pyrolysis performed in a fixed bed reactor shows no effect in promoting char yield. However, it is of interest to note that the char yield from pyrolysis of granulated tires was enhanced roughly 26% by oxygen pretreatment, as revealed in Table 5. As mentioned previously, this char yield enhancement may be attributable to the crosslinking between macromolecules in tire rubber due to the formation of oxygen functional groups during oxygen pretreatment. Oxygen pretreatment (at 140°C for 88 hours) of non-granulated tires shows little effect in increasing char yield. This may be due to the fact that oxygen cannot access the interior part of a large size tire rubber to promote the crosslinking between the molecules of the tire, or the pretreatment time was not long enough.

Tire pyrolysis performed under a mildly oxidizing (CO_2) condition was investigated. The comparison of char yields of tire pyrolysis in helium and CO_2 is shown in Fig. 5. These results show that char yields were higher when pyrolysis is carried out under a mildly oxidizing condition. Again, the existence of CO_2 during pyrolysis may provide oxygen to enhance the crosslinking reactions between tire molecules, and, therefore, increase the char yield. Since crosslinking enhancement has been mainly accomplished in the period of oxygen pretreatment, therefore pyrolysis carried out in CO_2 gives much less effect in the promotion of char yield for oxygen pretreated tires. Pyrolysis of non-granulated tires in CO_2 shows no effect in promoting char yield. This may also be due to the fact that CO_2 cannot easily diffuse into the interior part of a large piece of tire rubber to enhance the crosslinking reactions.

Zinc and sulfur have been reported to be the major components of the ash in tire chars [8,11]. Fig. 6 shows zinc and sulfur in the internal section of the solid residue from the pyrolysis of non-granulated tires in CO_2 , as measured by a SEM/X-ray microanalyzer. It shows, from the micrographs in Fig. 6, that zinc and sulfur grains are widely spread in the char and exist at the same locations, suggesting they are in a compound of zinc sulfide. Zinc sulfide is thought to be produced by the reaction between zinc oxide and the sulfur contained in tires [11].

Sulfur Distribution - Sulfur is used to cross link the polymer chains within the rubber. Therefore, due to environmental concerns, the emission of sulfur compounds from waste tire use has to be taken into account in the assessment of processes, such as tire pyrolysis, tire oil combustion, ..., etc. The distribution of sulfur in products after pyrolysis was investigated in this study. The sulfur contents of the gas and char from pyrolysis were determined by TG-FTIR and SEM/x-ray microanalysis, respectively. The quantity of sulfur contained in the liquid oil can be evaluated from the overall mass balance of sulfur of the tire pyrolysis. It is found that ~13% of tire sulfur is evolved in the gas phase ~9% is contained in the liquid oil, and ~78% is retained in the solid char. The results indicate that the sulfur within tire is preferentially retained in the char product after pyrolysis, since the char yield is typically 40% of the tire mass. This would imply that the cost of sulfur pollution control would be low in tire pyrolysis and for various uses of the tire oil.

High Pressure Treatments - High pressure treatment of automotive tires may hopefully result in the liquefaction of tire rubber and the recovery of carbon black. Table 6 presents the results obtained from wet and dry high pressure treatment of granulated tires. The overall mass balance is not 100% in Table 6. This deficiency in mass balance was also observed by Funazukuri et al. [12] in supercritical extraction of tire with water. The mass loss may be due to the evaporation of low boiling point oils during the process of product separation (separating solid and liquid). The product composition of wet and dry high pressure treatment are similar, and it shows roughly 35.9 ± 0.8 wt% solid residue, 45.4 ± 1.7 wt% oil, and 2.44 ± 0.89 wt% gas. The gaseous product is composed of CO_2 , CO , C_2H_4 , C_2H_6 and CH_4 , and its composition is shown in Table 7.

The results in Table 7 indicate that CO_2 is the main component of the gaseous products. The FT-IR absorbance spectra of the oils from high pressure treatment of tire are shown in Fig. 7, and the results of quantitative functional group analysis are shown in Table 8. Fig. 7 and Table 8 reveal that the property of the oils from high pressure treatment of tire is similar to that from tire pyrolysis shown in Fig. 4.

The solid residues from high pressure treatment (wet or dry) of tire contain carbon black, solid hydrocarbons and ash. The above results show that high pressure (wet or dry) pyrolysis of tires at low temperatures ($<400^{\circ}\text{C}$) is an alternative approach if recovery of carbon black or fuel oils is the primary objective. However, additional analysis is required of the solid material recovered in order to confirm this conclusion.

3. Surface Area Analysis

Unactivated Tire Chars - Fig. 8 shows the surface areas of the chars formed from the pyrolysis of the granulated tire sample in helium up to 500 and 700°C at a heating rate of $30^{\circ}\text{C}/\text{min.}$, and up to 900°C at various heating rates. The surface areas can be seen to increase with pyrolysis temperature. This result is in agreement with that of Williams et al. [8]. This observation says that chars prepared at lower temperatures retain a higher fraction of volatile material, resulting in lower surface areas. On the other hand, it is revealed in Fig. 8, that the surface area decreases with heating rate, and this trend is opposite to that observed in the study of Williams et al. [6]. As mentioned previously, this disagreement may be due to no holding period at final temperatures in our study.

Pyrolysis of non-granulated tires in helium up to 900°C also produced a char with a surface area of $97\text{ m}^2/\text{g}$. Surface areas of tire chars produced from the pyrolysis of both granulated and non-granulated tires in CO_2 were analyzed, and it shows no effect of CO_2 on the surface areas of char products. Pyrolysis of tires in a fixed bed reactor up to 700°C gave a char having a surface area of $79\text{ m}^2/\text{g}$, showing no significant improvement on creating char surface area. The surface area of char formed from the pyrolysis of O_2 pretreated tires in helium up to 900°C was measured, and it was found that the surface area of O_2 treated tire char was as high as $179\text{ m}^2/\text{g}$, which is almost twice as much as that of char from tires without any pretreatment under identical pyrolysis condition. Also, in the previous section, it showed that pyrolysis of O_2 treated tire gave the highest char yield. Therefore, considering both surface area and char yield, O_2 pretreatment of tires is very beneficial in producing high total surface area (in units of $\text{m}^2/(\text{g tire})$) carbon.

Fig. 9 shows the scanning electron micrographs of chars formed from pyrolysis of O_2 treated tires and tires with no pretreatment. It shows that the O_2 treated tire char has a very rough and dented surface, indicating that crosslinking or polymerization between rubber molecule and carbon black was enhanced by O_2 treatment and, therefore, the rubbers could not be totally volatilized during pyrolysis. On the other hand, the char from tires without any treatment shows a very smooth surface, indicating that most of the rubbers were volatilized during pyrolysis and the solid residue contains mainly carbon black and ash. The difference of char surfaces shown in Fig. 9 explains the higher surface area and yield of char produced from O_2 treated tires.

The above results show that the surface areas of chars formed from tire pyrolysis are comparable with the surface areas of carbon blacks in rubber products, including tires [7]. However, use of the char as activated carbon is not possible since commercial activated carbon has a higher surface area. An activation process is thus required for producing activated carbon from tire chars.

Activated Tire Chars - The surface areas of tire chars activated in CO_2 for various extents of burn-off are summarized in Table 9. It shows that the surface areas of tire chars increase monotonically with char burn-off, and pyrolysis conditions (including pyrolysis temperature, heating rate and gas environment) have little effect on the ultimate surface areas of activated tire chars. For granulated samples, similar to the results of unactivated chars, the O_2 treated tire chars gave the highest surface areas, i.e., up to $370\text{ m}^2/\text{g}$ at 50% burn-off.

Table 9 shows that non-granulated samples gave much higher surface areas than the granulated. This can be attributable to the higher ash contents of granulated samples, since the surface area of ash is very low ($8.6\text{ m}^2/\text{g}$). Having the value of ash surface area and the ash content allows us to calculate the specific surface area of dry ash free (d.a.f.) char. The calculated values for d.a.f. chars are also shown in Table 9. Table 9 reveals that the surface areas of granulated samples in terms of

daf mass are comparable to those of non-granulated samples. This is reasonable, since they were all derived from the same material.

For non-granulated samples, there was little size effect on surface areas of the activated chars, as revealed in Table 9. O_2 pretreatment of tires indeed increase the surface area of activated non-granulated char, but not as significantly as in the case of the granulated sample. Table 9 also shows that the surface area of non-granulated char was increased by performing activation under a higher partial pressure of CO_2 . Similar behavior was also reported for tire char activation in steam [11].

Torikai et al. [10] produced activated carbon from automotive tires by pyrolysis of the samples in an inert environment and activating the solid residue in a stream of CO_2 at $900^\circ C$. This activated carbon had surface areas of up to $400\text{ m}^2/\text{g}$ at 80% burn-off. Ogasawara et al. [11] prepared activated carbon from automotive tires from a wet thermal decomposition, and a $1260\text{ m}^2/\text{g}$ of carbon residue is obtained, however, with a yield of only 9 wt.% of the original tire sample. The total surface area of their product is $113\text{ m}^2/(\text{g tire})$. In our study, $813\text{ m}^2/\text{g}$ of activated carbon was produced with a yield of 17 wt.% of the original tire sample. The total surface area of this activated carbon was up to $138\text{ m}^2/(\text{g tire})$, a 20% increase when compared to the results of Ogasawara et al. [11]. This improvement could be partly due to differences in the starting tire samples.

The total surface area in units of $\text{m}^2/(\text{g tire})$ is actually a measure of activation (or burn-off) efficiency for producing activated carbon from tires. Fig. 10 shows the values of total surface area at various char burn-off. It shows no significant change with burn-off for granulated sample, indicating a low activation efficiency at higher burn-off. However, the total surface area of non-granulated sample increases significantly with carbon burn-off, indicating that the activation efficiency is high for this case. The reason for the better activation results for the char derived from larger tire pieces is not known. Since pyrolysis occurs from the outside of the particle to the center, a char layer will progressively move inward for larger pieces as the pyrolysis becomes less isothermal. This phenomenon may affect the development of the char morphology which in turn will affect how the material response to the activation process. This will be the subject of additional research.

CONCLUSIONS

1. Pyrolysis of granulated and non-granulated tires has shown recoveries of gases, liquid oils and solid char. The product yields vary with the variation of pyrolysis condition and pretreatment. The total yield of gases and tars increases with temperature up to $650^\circ C$, after which there is no significant change in product yield. The main gases evolved are H_2O , CH_4 , CO_2 , CO , SO_2 , C_2H_4 , and NH_3 . The derived oils are mostly aliphatic. The char yield increases with decreasing pyrolysis temperature and increasing heating rate. The char yield was found to be increased by performing pyrolysis under mildly oxidizing conditions, especially in the case of granulated tires. Both the gas and char yields of tire pyrolysis were increased by oxygen pretreatment, whereas the oil yield was reduced.
2. The sulfur within tires is preferentially retained in the char product after pyrolysis. This is an advantage for tire pyrolysis versus tire incineration, since the cost for sulfur emission controls would be low.
3. High pressure treatment of tires at low temperatures ($<400^\circ C$) is an alternative approach if recovery of carbon black or fuel oils is the primary objective.
4. The surface area of tire char is shown to increase with pyrolysis temperature and decrease with heating rate. O_2 pretreatment of tire shows beneficial results in promoting both char yield and surface area in tire pyrolysis, especially for granulated tires. The surface areas of tire chars are comparable with those of carbon blacks in rubber products, but too low if compared with that of commercial activated carbon. Therefore, an activation process is required for producing activated carbon from tire chars.

5. For production of a high specific surface area char directly from tire pyrolysis, the best results were obtained by O₂ pretreatment of granulated tires (~200 m²/g). However, in order to produce a commercial grade activated carbon an activation process is required and the efficiency of the activation process is best when non-granulated tire pieces are used. At 50% burnoff, specific surface areas close to 1000 m²/g (daf basis) were achieved in both cases. However, the net yield of activated carbon was significantly higher when starting with non-granulated tires. This is beneficial from an economic standpoint since the grinding costs are lower.

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Table 1. Composition of Tire Rubber [8,11]

Component	wt.% (as-received)
SBR	60 - 65
Carbon Black	29 - 31
Zinc Oxide	1.9 - 3.3
Sulfur	1.1 - 2.1
Extender Oil	~2
Additives	~0.7

Table 2. Composition of a Granulated Tire Sample.

Proximate Analysis (wt.%) (as-received)		Ultimate Analysis	
Moisture	0.4		
Volatile Matters	63.6	C, wt.% d.a.f.	88.1
Fixed Carbon	22	H, wt.% d.a.f.	7.9
Ash	14	N, wt.% d.a.f.	0.5
		S, wt.% d.a.f.	2.1
TOTAL	100	O, wt.% d.a.f.	1.4

* Supplied by Huffman Laboratories (Wheat Ridge, CO).

Table 3. Product Yields From Pyrolysis of Tires and O₂ Treated Tires in an Inert Environment.

weight % (as received)									
	H ₂ O	CO ₂	CO	CH ₄	C ₂ H ₄	SO ₂	NH ₃	Tars*	Char
Granulated Tires	3.5	0.6	1.5	0.36	0.089	0.31	0.38	57	36
O ₂ Treated Granulated Tires	5.3	3.3	3.3	1.2	0.24	1.0	0.21	39	45

* Estimated from mass balance

Table 4. Functional Group Analysis of Liquid Oils Formed from Tire Pyrolysis.

weight % (dmmf)								
Hydrogen		Aromatic Hydrogen			Carbon	Oxygen		
H _{Al}	H _{OH}	1 Adj	2 Adj	3 or more	(Aliphatic)	O _{Carbonyl}	O _{OH}	O _{Other}
13	0.045	0.44	0.44	0.40	81	0.84	0.75	0.58

Table 5. Product Yields (as-received basis) from Tire Pyrolysis in Helium Under Different Conditions

PYROLYSIS CONDITIONS								
Temp (°C)	Ramp (°C/min)	Pressure (atm)	Size	Reactor	Pretreat	Char Yield (%)	Gas (%)	Oil ⁺ (%)
500	30	1	granu.	TG	—	40	4.7	56
700	30	1	granu.	TG	—	38	5.6	57
900	20,000	1	granu.	Wire-Grid	—	38	—	—
900	100	1	granu.	TG	—	37	6.8	56
900	30	1	granu.	TG	—	36	7.0	57
900	3	1	granu.	TG	—	35	7.4	57
900	30	1	granu.	TG	Oxygen	45	15	39
700	30	1	granu.	Fixed Bed	—	37	—	—
900	30	1	non-granu.	TG	—	34	3.8	62
900	30	1	non-granu.	TG	Oxygen	35	—	—

⁺ Estimated from mass balance.

Table 6. Product Yields (as-received basis) of High Pressure Treatment of Tires.

	Solid (%)	Liquid (%)	Gas (%)	Mass Balance (%)
Wet	36.6	43.7	3.32	83.6
Dry	35.1	47.0	1.55	83.7

Table 7. The Gaseous Product Composition (by volume) from High Pressure Treatment of Tires

	CO ₂ (%)	CO (%)	C ₂ H ₂ (%)	C ₂ H ₄ (%)	CH ₄ (%)
Wet	90.6	—	2.9	3.8	2.6
Dry	60.3	8.7	9.0	13.5	8.5

Table 8. Functional Group Analysis of Liquid Oils Formed from High Pressure Treatments of Tires.

weight % (dmmf)									
	Hydrogen		Aromatic Hydrogen			Carbon	Oxygen		
	H _{at}	H _{OH}	1 Adj	2 Adj	3 or more	(Aliphatic)	O _{Carbonyl}	O _{OH}	O _{ether}
Wet	13	0.045	0.18	0.37	0.40	76	1.0	0.75	0.65
Dry	13	0.040	0.14	0.38	0.40	80	0.79	0.65	0.23

Table 9. Surface Areas of Tire Chars and Activated Tire Chars

SUMMARY OF RESULTS													
PYROLYSIS CONDITIONS								SURFACE AREA					
Temp °C	M °C/min.	Press ATM	Size	Gas	Reactor	Pretreat	Char Yield ^a (%)	M ² /g (as-received)			M ² /g,daf (daf)		
								0%	30%	50%	0%	30%	50%
500	30	1	P	He	TG	—	40	41	135	—	58	261	—
700	30	1	P	He	TG	—	38	69	134	—	104	273	—
900	20000	1	P	He	Wire-Grid	—	38	57	—	293	85	—	1089
900	100	1	P	He	TG	—	37	85	117	—	131	245	—
900	30	1	P	He	TG	—	36	99	124	188	157	268	815
900	30	1	P	CO ₂	TG	—	37	78	—	185	120	—	734
900	3	1	P	He	TG	—	35	98	125	—	158	280	—
900	30	1	P	He	TG	O ₂	45	179	252	357	256	447	930
900	30	1	P	CO ₂	TG	O ₂	45	—	—	365	—	—	952
700	30	1	P	He	Fixed Bed	—	37	79	126	—	122	264	—
900	30	1	L	He	TG	—	34	97	—	732	105	—	882
900	30	1	L*	CO ₂	TG	—	34	113	423	703	123	481	847
900	30	1	L	CO ₂	TG	O ₂	35	—	—	793	—	—	952
900	30	1	L	CO ₂ ⁺	TG	—	34	—	—	813	—	—	980

^a As-received basis.

* Smaller piece of non-granulated tire (10 mg).

⁺ Higher CO₂ partial pressure (1 atm).

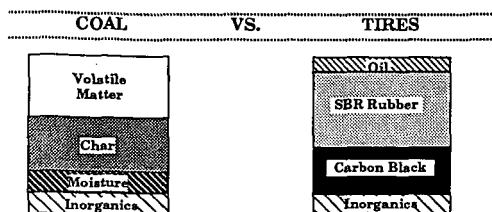
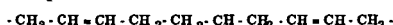
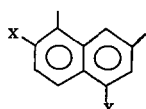


Figure 1. Comparison of Structure and Composition Between Coal and Tire Rubber.



ELEMENTAL ANALYSIS

C	82	C	88
H	5.5	H	8
O	8	O	2
N	1.7	N	0.5
S	2.4	S	1.5

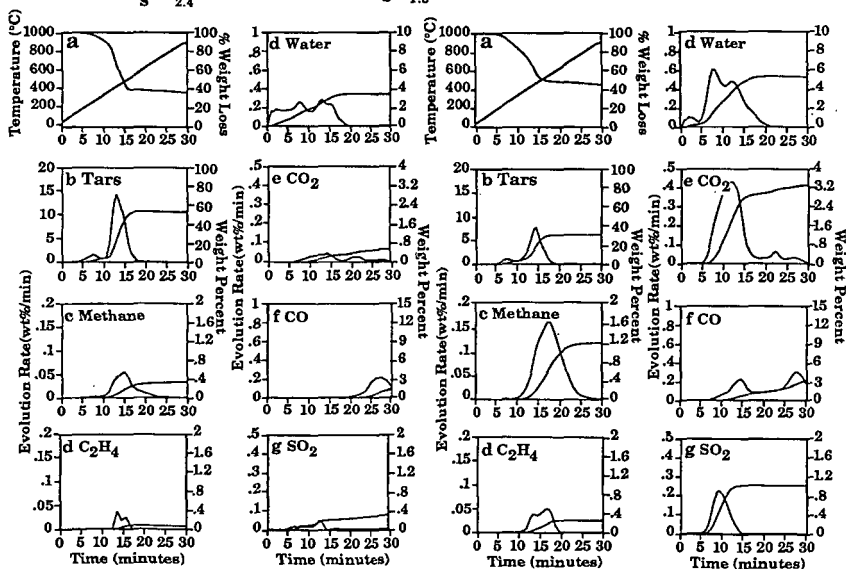


Figure 2. Product Evolution During the Pyrolysis Cycle of Granulated Tires.

Figure 3. Product Evolution During the Pyrolysis Cycle of the Oxygen Pretreated Tires.

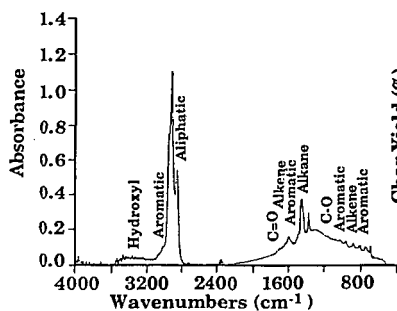


Figure 4. FT-IR Absorbance Spectrum of the Oils from Tire Pyrolysis.

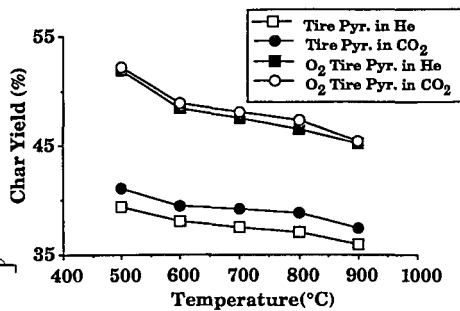


Figure 5. Comparison of Char Yields of Tire Pyrolysis in Helium and CO₂.

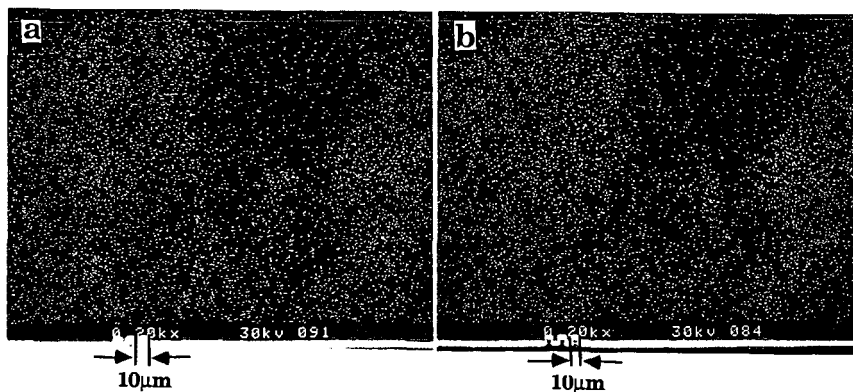


Figure 6. SEM/X-Ray Microanalysis of Zinc and Sulfur in a Carbon Residue. a) Zinc; b) Sulfur.

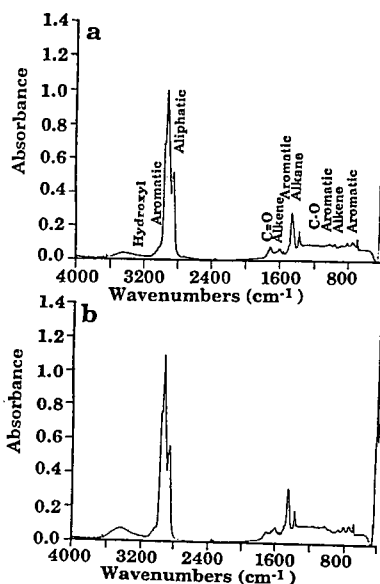


Figure 7. FT-IR Absorbance Spectra of Oils from High Pressure Treatments of Tires. a) Wet Process; b) Dry Process.

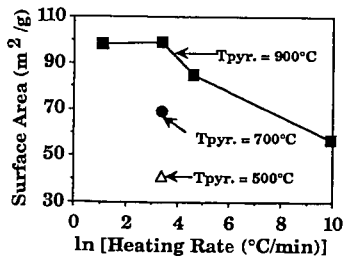


Figure 8. Surface Areas of Chars Formed from Different Pyrolysis Conditions.

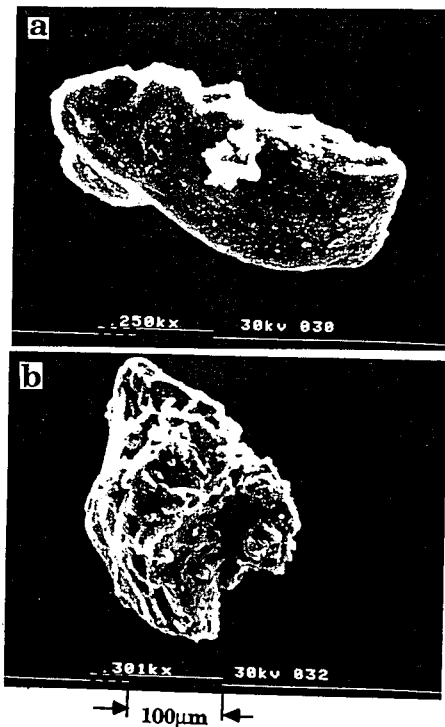


Figure 9. Scanning Electron Micrograph of 900°C Tire Chars from Tires. a) Without Pretreatment; b) Treated with Oxygen.

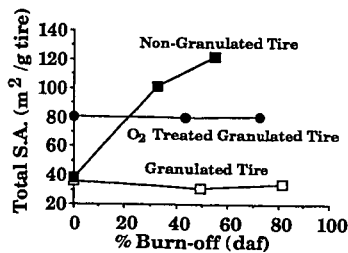


Figure 10. Total Surface Areas of Tire Chars at Various Extents of Carbon Burn-off.